Abstract

Metal oxides are attracting significant attention during the past decade as functional materials in the realms of both thin films and nanomaterials in view of a range of diverse and fascinating properties they display. The high temperature superconductivity (HTSC), colossal magnetoresistance (CMR), ferroelectricity and multiferroicity are few examples that have been constantly rejuvenating this field for more than a few decades. The wide spectrum of applications of metal oxides fall into the category of four major challenges to any mankind and civilization i.e. Energy, Health, Environment and Security. However, the oxide systems have been acquiring great practical importance in electronic materials as the device miniaturization is continued in microelectronics. The important discoveries in oxides had to wait for long time for practical applications due to technological challenge of being able to grow high quality oxide thin films and heterostructures. Therefore extensive research work was done on exploring the properties of thin films, hetero-structures and multi-layers involving these oxide systems and a considerable progress has been made in this direction. Most advanced device systems have a number of ultrathin layers grown under mutually compatible conditions. The surface effects in thin film such as mechanical stress, surface misfit, mono-atomic steps and grain boundaries (GBs) are important factors influencing the surface properties significantly. As the successive layers are grown, these effects get buried in any heterostructure. In addition to that the interfacial science of metal oxides is very fascinating due to an interesting interplay between charge, orbital, spin and lattice degree of freedoms across the interface. The electron bandwidth in oxides controls band bending near the interface which is quite different than conventional semiconductors. Therefore, the study of surface and interfacial effects in metal oxides is extremely important. The general interest of the present study has been to explore the surface and interfacial effects in some spintronic oxides i.e the half metallic CMR manganite, multiferroic BiFeO$_3$ (BFO), high mobility LaAlO$_3$ (LAO)-SrTiO$_3$ (STO) interfaces and spin filter CoFe$_2$O$_4$ (CFO) thin films and heterostructures, with an emphasis on the information obtainable by scanning probe microscopy (SPM) techniques.
1. Specifically, these effects were studied locally in strongly correlated CMR manganites thin films wherein the Mn-O-Mn bond property modulation can lead to a dramatically rich electronic and magnetic phase diagram. Manganites are also promising candidates for future spintronic devices due to CMR effect and half metallic character. The compound La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) is very important due to high spin polarization with highest Curie temperature ($T_c \sim 360$ K) among all manganite family. We have demonstrated the ultra thin films of LSMO (5 nm) show a significant change in Curie temperature ($T_C \sim 250$ K) due to stronger strain effects. Also, the electronic states near the edge of a unit cell step on the surface of these films examined by the STM/STS techniques showed a strong nanoscale modulation in the vicinity of unit cell steps on the surface. In the deep metallic ferromagnetic state at low temperature, the step related modulation progressively weakens but well defined pseudogap was detected in the density of states (DOS) probed by tunneling spectroscopy which also changes at the step edge working as defective site. The pseudogap is originated from strong electron phonon coupling and polaronic transport in these systems. The effect of surface topography and grain boundaries on the local electronic transport are examined by scanning probe microscopy. The surface topography shows a clear change from aligned fine grains to flat terraces after annealing with a large reduction of gap observed in tunneling spectroscopy. The conducting AFM studies revealed the conducting path networks and electronic inhomogeneities near the grains boundaries.

2. In the second set of experiments, the interfaces effects have been studied in the heterostructures of multiferroic BiFeO$_3$ - ferromagnetic La$_{0.67}$Sr$_{0.33}$MnO$_3$, high mobility LaAlO$_3$-SrTiO$_3$, and the spin filter CoFe$_2$O$_4$ - ferromagnetic La$_{0.67}$Sr$_{0.33}$MnO$_3$. The important finding is the resistance switching (RS) phenomenon at the interfaces of BiFeO$_3$ and CoFe$_2$O$_4$ with La$_{0.67}$Sr$_{0.33}$MnO$_3$. This phenomenon is very important for the development of oxide based non-volatile high-density memories at low cost. This phenomenon has been observed in a wide variety of other transition metal oxides without and with doping but the underlying switching mechanism is still unknown and controversial. The focus of current study is also to understand the switching mechanism using scanning probe microscopy techniques, which has emerged as a very powerful tool for the development of future technologies of writing and reading the bits with a very
high spatial resolution. We have demonstrated that the fresh interfaces between BFO-LSMO and CFO-LSMO show a resistive switching in current-voltage characteristics in current perpendicular to plane (CPP) configuration. The fitting of experimental results by interlayer transport mechanism shows the resistive switching to be of interfacial type and not filament-based. The concurrent measurements by piezoresponse and conducting atomic force microscopy on the BFO-LSMO system reveals that the resistance switching from low to high resistive state (or vice versa) occurs via polarization switching inside the BFO layer controlling the properties at the interface. On the other hand, the charge distribution of a CFO-LSMO interface undergoes an electronic reconstruction from uniform nanoscopic electronic inhomogeneities near grain boundaries to large scale electronic inhomogeneities after switching. The scanning tunneling spectroscopy results suggests that polaron trapping may lead to electronic inhomogeneities responsible for hysteresis and resistive switching.

3. The interfaces of LaAlO$_3$ and SrTiO$_3$ are studied using temperature dependent scanning tunneling spectroscopy (STS). The energy gap gradually opens in the density of states (DOS) as the temperature is lowered. These studies reveal strong correlation effects at low temperature in agreement with the reported theoretical electronic states calculations.